

The Inhibition of Butyl Acrylate by *p*-Methoxyphenol

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SYNOPSIS

The lengths of polymerization induction periods for butyl acrylate (BA) in the presence of air were measured at temperatures from 54 to 122.5°C. The kinetics of MEHQ and oxygen consumption at 80 and 100°C are characterized by their own induction periods followed by sharply accelerated rates immediately prior to the BA polymerization. It is proposed that these phenomena are consistent with an "intrinsic" BA radical formation rate that is extremely slow compared to the ultimate rate of radical production from the decomposition of peroxides. These oligomeric peroxides build up during the induction period and, at its end, rapidly decompose with a resulting "radical cascade effect," causing the accelerated inhibitor and oxygen consumption followed rapidly by BA polymerization. Thus, confirmation that a supply of BA has a normal MEHQ concentration may not be sufficient to ensure its stability. Strict adherence to the storage conditions and shelf life recommended by the supplier⁶ is absolutely vital to storage safety, especially because uncontrolled polymerization of BA has the potential to be violent (polymerization exotherm rates higher than 1000°C/min were observed). © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Certain alkyl esters of acrylic acid (i.e., methyl, ethyl, butyl, and 2-ethylhexyl acrylates) are widely used as monomers in the paint, coatings, and latex industries, and butyl acrylate (BA) is one of the more frequently used of these esters. Commercial BA is typically inhibited with 1.09×10^{-4} mol/L (15 ppm by weight) *p*-methoxyphenol (MEHQ, monomethyl ether of hydroquinone). Although acrylic acid esters are generally regarded as being more stable towards polymerization than the parent acid, very little work has been reported that actually characterizes the chemistry and kinetics of the inhibition of polymerization in these esters. We wanted to determine whether the greater stability attributed to these esters is manifested through longer induction periods, slower rates of polymerization, or both. Because we have previously studied the chemistry and kinetics of inhibition of acrylic acid (AA) by MEHQ,^{1,2} we felt that a comparison of the corresponding characteristics of BA would be useful. The experimental observations reported here show that these char-

acteristics (i.e., length of induction periods and rates of inhibitor and oxygen consumption) are very different from those of AA. We also suggest a mechanistic rationale that is shown to be consistent with the kinetic characteristics by use of a mathematical model.

EXPERIMENTAL

The analytical method used for determining MEHQ concentrations as well as a description of the vessels used to determine polymerization induction periods have been described previously.¹

The method used to measure the oxygen uptake rates of BA using a gyrotory water bath shaker was described previously.² Other flasks containing BA samples used for parallel MEHQ analyses and induction period determinations were placed in the gyrotory bath along with the flask used for the manometric measurements.

Calorimetry experiments were run using a Reactive System Screening Tool (RSST) calorimeter as described previously.³

RESULTS AND DISCUSSION

Polymerization Induction Periods

Polymerization induction periods of BA stabilized with 1.09×10^{-4} mol/L MEHQ were measured at temperatures ranging from 54 to 122.5°C in the presence of air. These determinations were carried out in three different types of equipment: special sample tubes, the RSST calorimeter, and flasks placed in the gyrotory water bath (see references in the Experimental Section). In each case the sample had access to unlimited amounts of air so that the onset of polymerization would not be caused by oxygen depletion. The results are shown in Table I and plotted in "inverse" Arrhenius format in Figure 1. Linear regression of the data gives the equation:

$$t_i = 7.02 \times 10^{-16} \exp(28400/RT)$$

where t_i is the polymerization induction period in hours, R the gas constant in cal mol⁻¹ K⁻¹, and T the temperature in Kelvin.

Polymerization Exotherm Rates

Four of the induction period determinations (96 to 122.5°C) were carried out in an RSST calorimeter (see Experimental Section), so that exotherm rates could also be measured. In all four runs, maximum instantaneous temperature rates of well over 1000°C/min were measured. Comparing these results to those obtained for AA stabilized with 1.71×10^{-3} mol/L MEHQ (200 ppm by weight),¹ we find that the induction periods for BA polymerization are longer by a factor of about 3 to 6 but the

Table I Polymerization Induction Periods of Butyl Acrylate Stabilized with 1.09×10^{-3} mol/L (15 ppm) MEHQ in Air

Temperature, °C	Induction Period, h
122.5	3.82
122.5	2.96
112.6	9.40
101.6	25.2
100.3	22.3
101.3	20.7
99.6	23.8
96.0	79.6
80.0	446
80.0	435
80.0	486
54.0	3666

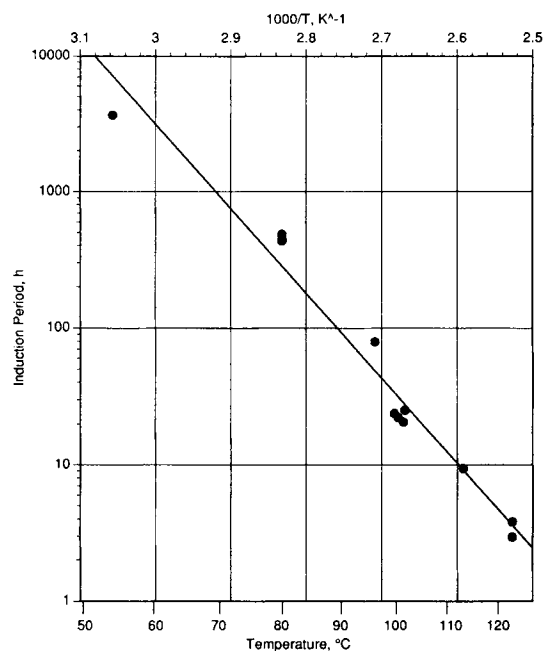


Figure 1 Polymerization induction periods for butyl acrylate inhibited with 1.09×10^{-4} mol/L MEHQ.

polymerization exotherm rates of BA are just as rapid as those of AA. Hence, BA may be regarded as being more stable than AA, but only in the heating time required before polymerization begins. Once polymerization begins, BA has the potential to undergo just as vigorous a thermal runaway as AA. (We have previously reached analogous conclusions regarding the stability of vinyl acetate relative to that of AA³.)

Calorimetry was carried out on a sample of BA containing 1.09×10^{-4} mol/L MEHQ held at 122°C with the careful exclusion of oxygen from the system. A barely detectable exotherm began after about 1 h and lasted for 5 h. When the calorimeter was opened, the sample was found to have completely polymerized. This foreshortening of induction period with marked decrease in the polymerization rate is directionally the same effect that oxygen exclusion has on AA.¹

Inhibitor Disappearance Rates

The rate of disappearance of MEHQ from BA containing an initial MEHQ concentration of 1.09×10^{-4} mol/L was measured at 80°C with the sample in a gyrotory water bath shaker so that it was constantly saturated with air. Surprisingly, the MEHQ concentration did not change very much over a period of about 250 h, after which time it started dropping at an accelerated rate (see Fig. 2). The last

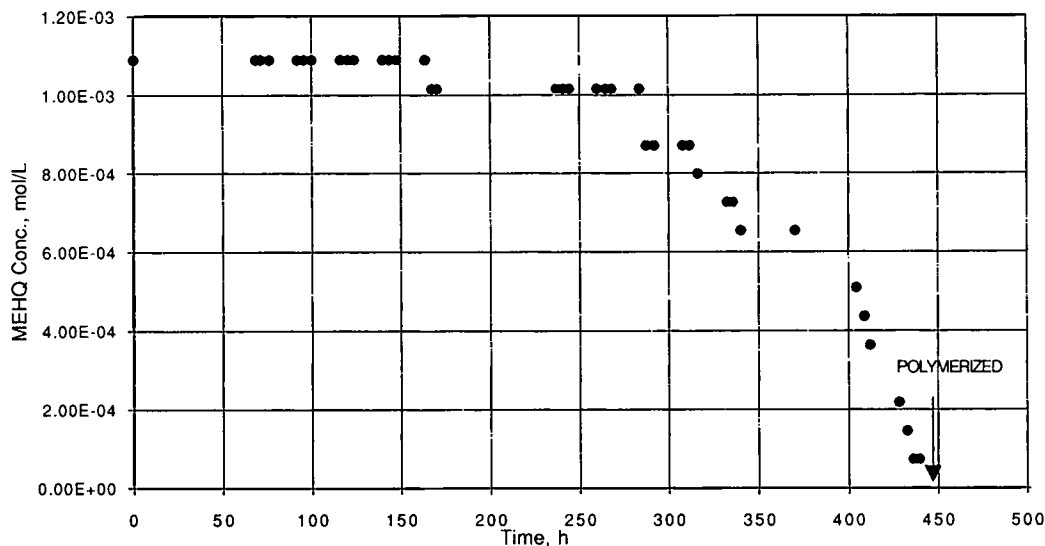


Figure 2 Rate of MEHQ disappearance from butyl acrylate inhibited with 1.09×10^{-4} mol/L MEHQ at 80°C .

aliquot sample was taken at 440 h and was found to contain 7.27×10^{-6} mol/L (1 ppm) MEHQ. The BA polymerized sometime within the next 12 h. In another determination, a sample of BA initially containing 1.51×10^{-3} mol/L MEHQ was heated at 80°C for 320 h, during which time no drop in the MEHQ concentration was detected.

BA containing 1.09×10^{-4} mol/L MEHQ was heated at 100°C in air and the MEHQ concentration again followed. It remained fairly constant for about 12 h, after which it decreased at an accelerated rate followed by BA polymerization at 23 h (see Fig. 3). A sample of BA containing an initial MEHQ concentration of 6.69×10^{-4} mol/L was heated in air at 100°C . Aside from an unexplained drop of about

1.45×10^{-4} mol/L MEHQ concentration at 63 h (perhaps due to an analytical calibration shift), the MEHQ concentration held steady until it dropped precipitously after 140 h (Fig. 4). Polymerization took place at 154 h.

Oxygen Absorption Rates

In the determination of BA oxygen uptake at 80°C , a sample containing 1.09×10^{-4} mol/L MEHQ was heated for about 350 h without any appreciable oxygen uptake, at which time the oxygen uptake began markedly accelerating. The sample polymerized at 486 h (see Fig. 5). Essentially the same results were obtained in a duplicate determination, in which the polymerization took place after 436 h.

In another experiment, BA inhibited with 1.45×10^{-3} mol/L MEHQ was heated to 80°C for 500 h without any detectable uptake of oxygen.

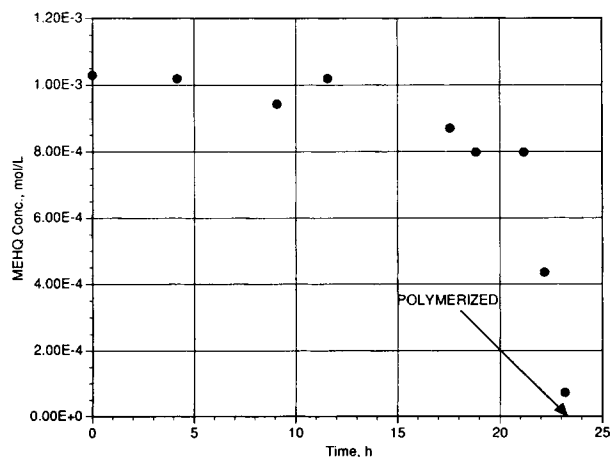


Figure 3 Rate of MEHQ disappearance from butyl acrylate inhibited with 1.09×10^{-4} mol/L MEHQ at 100°C .

Mechanism

The configuration of the curves describing the rates of MEHQ consumption and oxygen uptake in BA match each other fairly well: neither exhibits any measurable rate for an extended time, after which both rates markedly accelerate to high values and the BA polymerizes. This behavior is in marked contrast to the essentially pseudo-zero-order rates observed in acrylic acid.^{1,2} A possible explanation for the "flat+accelerated" rates in BA is that there is an impurity present that acts as a strong primary radical trap, competing successfully with oxygen and

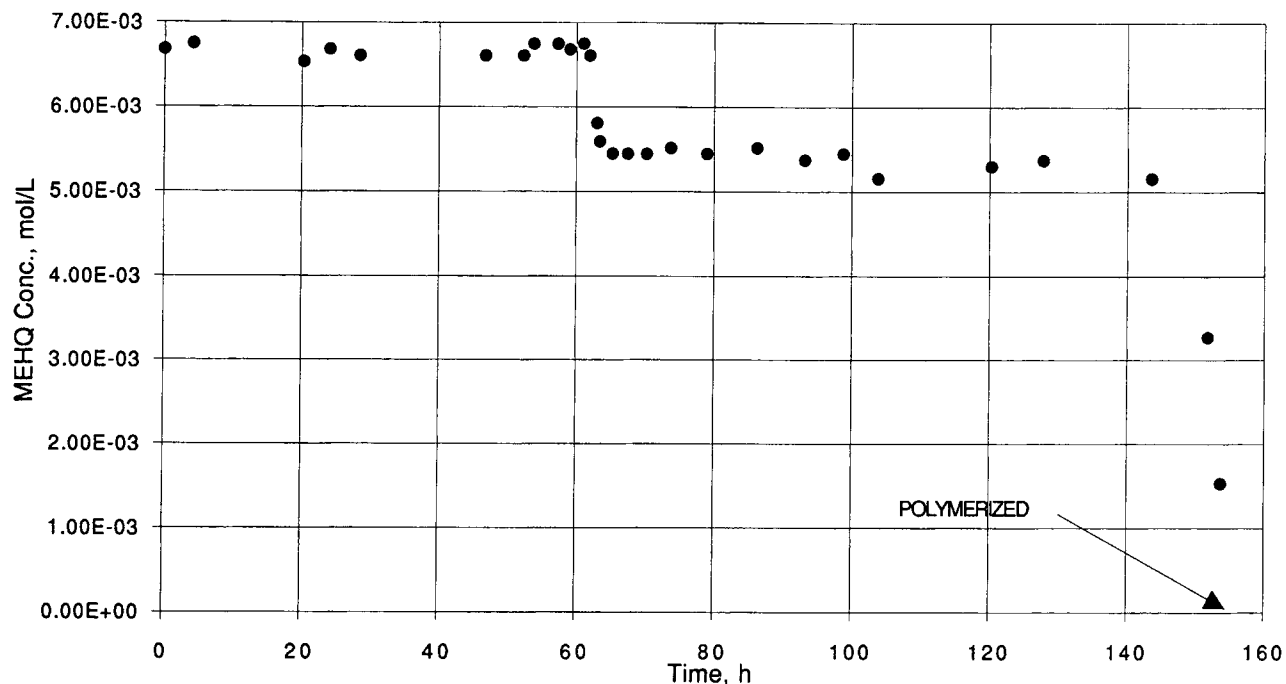


Figure 4 Rate of MEHQ disappearance from butyl acrylate inhibited with 6.69×10^{-4} mol/L MEHQ at 100°C .

MEHQ for these radicals. When this impurity is exhausted through its reaction with radicals, the MEHQ, a weaker inhibitor that traps oxygen-centered radicals, "takes over," allowing the radicals to first react with molecular oxygen before it traps them. Only at this point would the consumption of MEHQ and oxygen be observed.

This impurity theory was tested by removing the MEHQ (a crystalline solid) from a sample of commercial BA by flash distillation. Any impurities in the BA would be expected to have flashed along with the monomer because high-boiling by-products are removed very efficiently during plant purification. Samples of the MEHQ-free BA were heated at

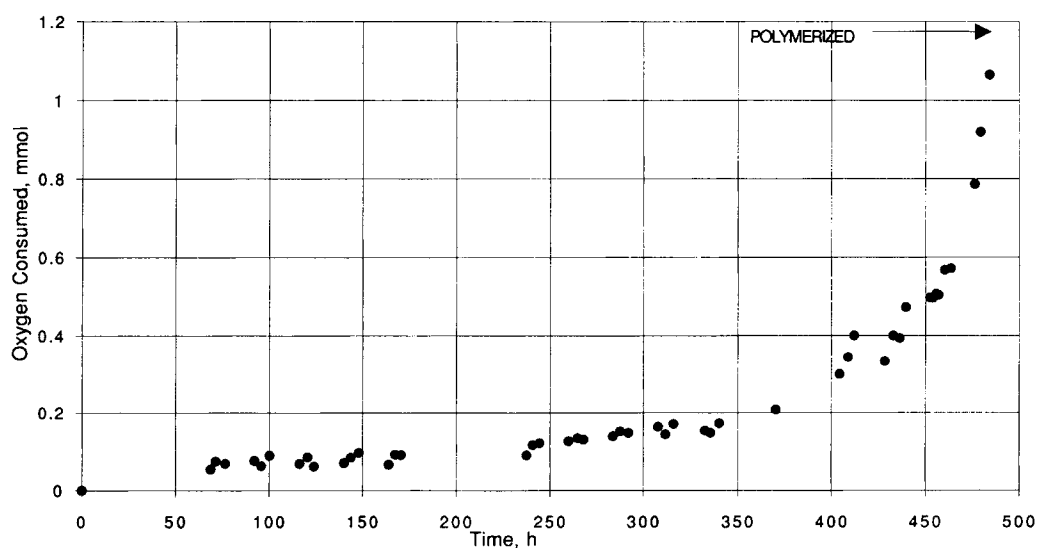
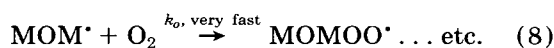
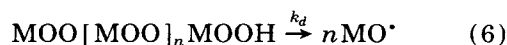
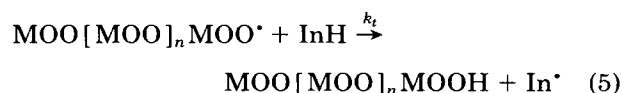
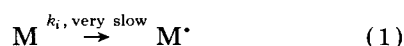


Figure 5 Rate of oxygen absorption by butyl acrylate inhibited with 1.09×10^{-4} mol/L MEHQ at 80°C .

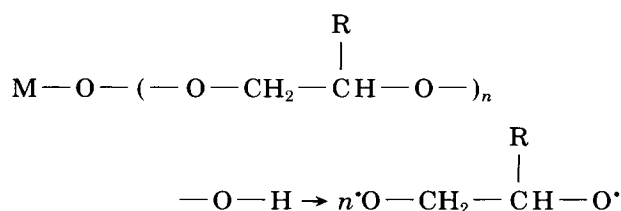
100°C in the presence of air. The average induction period to polymerization observed in these samples was 15 min compared to about 23 h when MEHQ is present. If most of the 23 h induction period were due to an impurity, one would expect to observe a significant part of the induction period even when the MEHQ is removed. Because this was not the case, we conclude that the impurity theory is extremely improbable.

There is a set of kinetic circumstances that can explain the shape of the MEHQ and oxygen consumption kinetic curves without appeal to a radical-trapping impurity. The pseudozero-order rates of oxygen and MEHQ consumption during the induction period of AA fit a mechanistic scheme wherein there is a constant, detectable rate of carbon-centered radical formation in the monomer. These radicals react with dissolved oxygen to form peroxy radicals that ultimately react with MEHQ. In other words, the "intrinsic" radical production mechanism in AA, whatever its nature may be, is the main source of initiation and any decomposition of peroxides is merely incidental, or perhaps occurs because of the exotherm of polymerization. Now, if a monomer had an extremely small intrinsic rate of radical production, the principal mechanism for radical formation could be via the "radical cascade effect" from the decomposition of peroxides (i.e., reaction of peroxide-derived radicals with monomer followed by reaction with oxygen, thus forming more peroxide, leading to more radicals, etc.). This mechanistic scheme is as follows:



In the above scheme, M is monomer, M* a carbon-centered radical, and InH inhibitor. The following rate constants are used: k_i for "intrinsic" radical

formation; k_o for radical reaction with dissolved oxygen (close to diffusion controlled rate), k_p for chain propagation, k_t for chain termination with inhibitor, and k_d for oligomeric peroxide decomposition to alkoxy radicals. In reality, the maximum number of oxygen radical centers available from the decomposition of an oligomeric peroxide of n units is $2n$. That is, each of the two backbone carbon atoms can bear an oxygen atom with an unpaired electron.



However, some of these potential oxygen radical centers, in fact, lead to carbonyl groups during decomposition of the peroxide,⁴ so assuming a radical yield of 50% (i.e., n instead of $2n$) is not unreasonable.

We propose that for BA, in contrast to AA, k_i is very small, so that the contribution of reaction 1 to the radical flux of the system is very minor. The principal source of radicals in the system is via the decomposition of oligomeric peroxide, which follows the rate law:

$$\frac{dMO^*}{dt} = \frac{(n) - d[\text{Peroxide}]}{dt} = -nk_d[\text{Peroxide}]$$

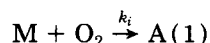
Initially, the peroxide concentration is relatively low, so that the rate of reaction 6 is negligible and, thus, the inhibitor and oxygen consumption rates are undetectable. Eventually, however, the peroxide concentration reaches a critical level and the value $k_d[\text{Peroxide}]$ becomes high enough for the rate of reaction 6 to become significant. The radical flux from the decomposition of the oligomeric peroxide pool then becomes high enough to start a highly branched, autocatalytic chain reaction ("radical cascade effect," reactions 7 and 8 and then 5 and 6), resulting in the accelerated consumption of oxygen and inhibitor, followed by rapid polymerization of the BA.

Mathematical Kinetic Model

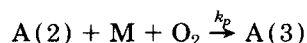
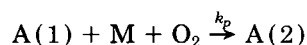
We felt that the above mechanistic concept would have added credibility if a simplified mechanistic model could be constructed, the kinetics of which qualitatively simulated the shape of the experimen-

tal concentration vs. time curves for MEHQ and oxygen consumption in BA. The simplified mechanism is shown below. For simplification, the first reaction is actually a combination of reactions 1 (slow intrinsic radical formation) and 2 (very rapid reaction of this radical with dissolved oxygen) in the mechanistic scheme shown earlier.

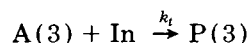
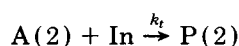
Initiation



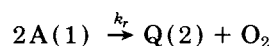
Propagation



Termination with Initiator

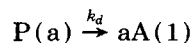


Radical-Radical Termination

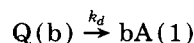


Similarly, all other possible radical-radical combinations from A(1) to A(3) producing Q(2) to Q(6).

Peroxide Decomposition



Where a = 1 to 3
and



where b = 2 to 6.

The symbols are as follows: M is monomer, A(m) is an oxygen-centered oligomeric radical (alkyl peroxy or alkoxy) of m (1 to 3) units; In is inhibitor; P(a) and Q(b) are oligomeric peroxides having a and b units, respectively. The Ps are made by radical-inhibitor terminations and the Qs by radical-radical terminations. A key feature of this scheme is the assumption that each peroxide bond breaks to give at least one A(1) radical. It is this high radical yield from peroxide together with a very low value for k_i , which leads to the flat+accelerated shape of the oxygen and MEHQ kinetic curves.

Numerical solutions to a complete set of differential kinetic equations describing this model reaction network were obtained using a Microsoft Excel spreadsheet with each row differing from the previous one by the chosen time interval, Δt .⁵ By empirically tuning the relative values of the rate constants for initiation (k_i), chain propagation (k_p), termination by inhibitor (k_t), radical-radical termination (k_r), and decomposition of peroxide (k_d), the experimentally observed flat+accelerated shape of the MEHQ and oxygen consumption curves could, indeed, be simulated. As postulated, when the assigned value of k_i was many orders of magnitude lower than the other rate constants (especially k_d), there was a slow buildup of peroxide with little change in oxygen or inhibitor concentration during an initial induction period. Once the peroxide concentration reached a critical value (about 3×10^{-4} mol/L), there was a marked acceleration of peroxide decomposition, in turn causing acceleration of the oxygen and inhibitor consumption rates, followed by BA polymerization. Figure 6 shows the plots of oxygen and inhibitor consumption vs. time generated by the model for the following values of the rate constants:

$$k_i = 6.0 \times 10^{-11} \text{ L mol}^{-1} \text{ h}^{-1}$$

$$k_p = 6.0 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ h}^{-1}$$

$$k_t = 24 \text{ L mol}^{-1} \text{ h}^{-1}$$

$$k_r = 3.0 \times 10^{-2} \text{ L mol}^{-1} \text{ h}^{-1}$$

$$k_d = 3.0 \times 10^{-3} \text{ h}^{-1}$$

$$\text{Time interval, } \Delta t = 2.8 \text{ h}$$

Practical Considerations

The polymerization induction period of BA is characterized by an essentially constant MEHQ concentration. The end of this induction period is signaled by a precipitous drop in that concentration before polymerization occurs. The MEHQ concentration profile probably has the same general shape when BA is aged at storage temperatures. For this reason, confirmation that a supply of BA has a normal MEHQ concentration may not be sufficient to ensure its stability. Strict adherence to the storage conditions and shelf life recommended by the supplier⁶ is absolutely vital to storage safety. Evidently, the only potentially detectable compositional change that occurs as a sample of BA ages is its

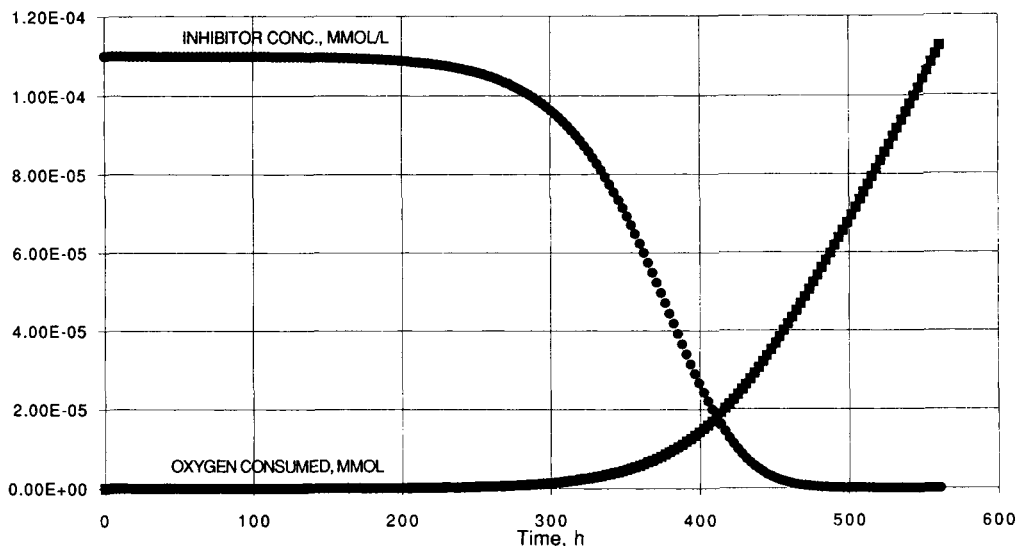


Figure 6 Rates of oxygen and inhibitor consumption in butyl acrylate calculated from the mathematical kinetic model.

peroxide content. Ideally, a very sensitive and accurate peroxide analysis should allow one to determine how far along the induction period curve (i.e., shelf life) a sample of BA has gone. It has been our experience, however, that published methods for the determination of oligomeric peroxides⁷ are not reliable for acrylic monomers; we are currently working on the development of a reliable method.

CONCLUSIONS

The kinetics of MEHQ and oxygen consumption during the polymerization induction period of BA in air at 80 and 100°C are characterized by their own induction periods followed by sharply accelerated rates immediately prior to polymerization. It is proposed that these phenomena are consistent with an "intrinsic" BA radical formation rate that is extremely slow compared to the ultimate rate of radical production from the decomposition of peroxides. These oligomeric peroxides build up during the induction period and, at its end, rapidly decompose with a resulting "radical cascade effect," causing accelerated inhibitor and oxygen consumption followed rapidly by BA polymerization. Thus, confirmation that a supply of BA has a normal MEHQ concentration may not be sufficient to ensure its stability. Strict adherence to the storage conditions and shelf life recommended by the supplier⁶ is ab-

solutely vital to storage safety, especially because uncontrolled polymerization of BA has the potential to be violent (polymerization exotherm rates higher than 1000°C/min were observed).

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